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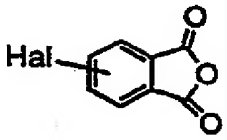
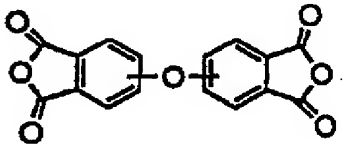
(54) Title: METHOD FOR PREPARING OXY–DIPHTHALIC ANHYDRIDES



(1)



(2)

(57) Abstract

Disclosed is a method for preparing oxy–diphthalic anhydrides, which comprises reacting a halo–phthalic anhydride represented by formula (1) where Hal represents F, Cl, Br or I, with a carbonate salt selected from the group consisting of lithium carbonate, sodium carbonate, magnesium carbonate and calcium carbonate in a solvent to prepare oxy–diphthalic anhydrides represented by formula (2).

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DESCRIPTION

METHOD FOR PREPARING OXY-DIPHTHALIC ANHYDRIDES

Field of the invention

The present invention relates to a method for preparing oxy-diphthalic anhydrides. The oxy-diphthalic anhydride is important as a starting material for preparing polyimide(s) by reacting with various diamine(s).

Background art

Various methods for preparing oxy-diphthalic anhydrides have been described in literatures. In the old time, there was a method based on an oxidation reaction of tetramethylphenyl ether proposed by Marvel et al. (J. Am. Chem. Soc. 80, 1197-(1955)). This oxidation reaction is inappropriate from the view point of the industrial preparation, since potassium permanganate with high toxicity is employed as an oxidant. Further, in Japanese Provisional Patent Publication No. 122738/1978, there has been described a method for obtaining oxy-diphthalic anhydrides by reacting a halogenated (halo-) phthalic anhydride with caustic soda in a polar solvent, but the yield of the product prepared by this reaction is extremely low. Japanese Provisional Patent Publication Nos. 136246/1980 and 127343/1980 describe a method for preparing oxy-diphthalic anhydrides by reacting a nitro-phthalic anhydride with sodium nitrite and a carbonate salt in a polar solvent. These methods are hardly used for

industrial purposes since a harmful nitric oxide is by-produced during the reaction.

In Japanese Provisional Patent Publication No. 96183/1988, there has been disclosed a method for preparing oxy-diphthalic anhydrides by reacting a halo-phthalic anhydride with potassium carbonate and potassium fluoride or cesium fluoride in a polar solvent. However, this method is based on the reaction in which water participates, and can not provide a sufficient yield because of the low reaction ratio caused by the existence of water.

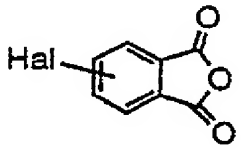
Japanese Patent Publication No. 50071/1991 discloses a method for obtaining oxy-diphthalic anhydrides by dehydrohalogenating a hydroxy-phthalic anhydride and a halo-phthalic anhydride in the presence of potassium carbonate. However, this method is required to prepare the hydroxy-phthalic anhydride by hydrolysis of a halo-phthalic anhydride, thus it can not be said to be an industrially advantageous preparation method.

In Japanese Provisional Patent Publication No. 254673/1989, there has been disclosed a method for directly preparing oxy-diphthalic anhydrides directly by reacting a halo-phthalic anhydride with potassium carbonate in the presence of a potassium fluoride catalyst. This method requires to stir carefully because this method is based on the neat reaction or the similar reaction thereto, thus it is difficult to allow the reactivity to stabilize. In addition, in this method, potassium carbonate can be used restrictedly, and when another carbonate salt such as

sodium carbonate is employed in place of potassium carbonate in this method, the reactant shows a high viscosity and the reaction cannot be completed because the reactant does not show any sufficient flowability.

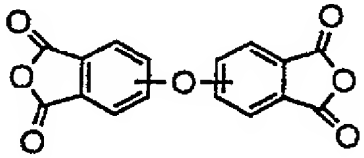
Summary of the invention

The present invention relates to a method for preparing oxy-diphthalic anhydrides, which comprises reacting a halo-phthalic anhydride represented by the formula (1):



(1)

where Hal represents F, Cl, Br or I,
with a carbonate salt selected from the group consisting of lithium carbonate, sodium carbonate, magnesium carbonate and calcium carbonate in a solvent to prepare oxy-diphthalic anhydrides represented by the formula (2):



(2)

Description of the preferred embodiments

According to the present invention, oxy-diphthalic anhydrides can be prepared by employing a carbonate salt

other than potassium carbonate and a solvent in the reaction. The shape of the carbonate salt may be powdery or granular, and preferably, the use of the granular carbonate salt leads to more effective reaction. For example, it has been found that the product can be obtained with the reaction ratio of 90% when granular sodium carbonate called typically "soda ash" is employed.

The carbonate salt which can be employed is selected from the group consisting of lithium carbonate, sodium carbonate, magnesium carbonate and calcium carbonate, and preferably sodium carbonate. Where the reaction is carried out in a solvent employing potassium carbonate, it can not provide the predetermined reaction ratio because the reaction cannot be completed. The shape of the carbonate salt, which can be employed in the method of the present invention, may be powdery or granular, and the preference is the granular carbonate salt having the diameter of preferably 50-750 μm and more preferably 150-750 m. From the view point of the yield, the molar ratio of the carbonate salt to the halo-phthalic anhydride is advantageously in the vicinity of about 0.5, and the preferred molar ratio is 0.5-0.4.

The reaction temperature, at which the method of the present invention is carried out, is generally within the range of 170-260°C. The employable catalyst is a phosphonium salt or a sulfonium salt which is a phase transfer catalyst capable of tolerating at the reaction temperature. Such a catalyst may includes, for example, triphenylphosphine, tetraphenylphosphonium bromide,

tetrabutylphosphonium chloride, triethylsulfonium iodide, triphenylsulfonium bromide, etc. The amount of the catalyst is 0.1-10 % by weight, preferably 0.3-5 % by weight, based on the halo-phthalic anhydride. Further, the use of an alkali-metal iodide or an alkali-metal fluoride as a co-catalyst allows the reactivity to heighten, and further there is also a merit that the product is little colored. The employable alkali-metal iodide includes LiI, NaI, KI, etc., and the employable alkali-metal fluoride includes LiF, NaF, KF, etc. The amount of the co-catalyst to be employed is 0.05-5 % by weight, preferably 0.1-2 % by weight, based on the halo-phthalic anhydride.

A solvent is employed in the reaction. The solvent to be employed must have a boiling point near the reaction temperature (170-260°C) and not participate in the reaction. For example, a polychlorobenzene such as 1,2-dichlorobenzene and 1,2,4-trichlorobenzene, a polychlorotoluene such as 1,2-dichlorotoluene can be employed. A dehydrated aprotic polar solvent, e.g., sulfolane can also be employed. The amount to be employed is 50-600 % by weight, preferably 100-200 % by weight, based on the halo-phthalic anhydride.

In order to isolate oxy-diphthalic anhydrides, the reaction product is subjected to hot filtering, followed by cooling the resulting filtrate to obtain oxy-diphthalic anhydrides. The filtrate may be concentrated if desired to allow the yield to increase. When sulfolane is employed, after allowing the filtrate to disperse in water, the precipitated oxy-diphthalic acid is subjected to the solid-

liquid separation. The resulting oxy-diphthalic acid is ring-closed by heating or employing acetic anhydride to obtain oxy-diphthalic anhydrides.

According to the method of the present invention, since the reaction is carried out in the presence of a solvent, it is hard to produce resin components and to color in comparison with the neat reaction, and therefore the method can save time and labor for decoloration and purification. Accordingly, oxy-diphthalic anhydrides, which are preferable also for the electronic material use where the high purity is required, can be obtained.

EXAMPLES

Example 1

90.8 g (0.4 mol) of 4-bromo-phthalic anhydride and 150 g of 1,2-dichlorotoluene were charged in a reactor to heat at 210°C. Then, 21.2 g (0.20 mol) of granular sodium carbonate having the diameter of 200-500 μm, 4.5 g (0.011 mol) of tetraphenylphosphonium bromide and 2.1 g (0.013 mol) of potassium iodide were charged in the reactor intermittently over 90 minutes, followed by aging for 3 hours after the charge. High performance liquid chromatography test showed 90% of the reaction ratio (yield). The reaction product was cooled to 150°C, followed by hot filtering. After cooling the filtrate, 4-oxy-diphthalic anhydride was isolated (amount: 50.9 g (yield: 82.0%)). Acetic acid is employable to wash if further purification of the product is needed.

Example 2

73.0 g (0.40 mol) of 3-chloro-phthalic anhydride and 200 g of 1,2,4-trichlorobenzene were charged in a reactor to heat at 220°C. Then, 14.8 g (0.20 mol) of granular lithium carbonate having the diameter of 200-500 μm, 3.5 g (0.015 mol) of triethylsulfonium iodide and 1.8 g (0.031 mol) of potassium fluoride were charged intermittently over 90 minutes, followed by aging for 4 hours after the charge. High performance liquid chromatography test showed 88% of the yield. The reaction product was cooled to 150°C, followed by hot filtering. After cooling the filtrate, 3-oxy-diphthalic anhydride was isolated (amount: 49.6 g (yield: 79.9%)). Acetic acid is employable to wash if further purification of the product is needed.

Example 3

90.8 g (0.40 mol) of 4-bromo-phthalic anhydride and 150 g of dehydrated sulfolane were charged in a reactor to heat at 200°C. Then, 21.2 g (0.20 mol) of granular sodium carbonate having the diameter of 200-500 μm, 4.5 g (0.017 mol) of triphenylphosphine and 2.1 g (0.013 mol) of potassium iodide were charged intermittently over 90 minutes, followed by aging for 4 hours after the charge. High performance liquid chromatography test showed 85% of the yield. The reaction product was cooled to 150℃, followed by hot filtering. The filtrate was subjected to cooling to charge in 500 ml of 5% aqueous acetic acid solution, followed by stirring with heat for 2 hours at

90°C in order to allow oxy-diphthalic anhydrides to ring-open to obtain a tetracarboxylic acid. After cooling, the product was subjected to the solid-liquid separation, followed by allowing the resulting oxy-diphthalic acid to ring-close by heating in 20 g of 1,2-dichlorobenzene for 3 hours at 220°C. When the ring-closure of the oxy-diphthalic acid has been completed, the state of the system changed from white turbid to the state between transparent and slightly turbid. After hot filtering the product, the filtrate was cooled, followed by isolating 4-oxy-diphthalic anhydride (amount: 49.0 g (yield: 79.0%)). Acetic acid is employable to wash if further purification of the product is needed.

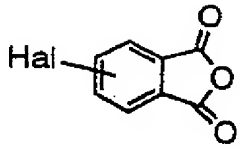
Comparative example 1

The reaction was carried out under the same conditions as in Example 1, except that the granular potassium carbonate having the diameter of 200-500 μm was employed in place of granular sodium carbonate. The yield of 4-oxy-diphthalic anhydride was 37.1%.

Thus, in comparison with the reaction in which potassium carbonate was employed in the solvent, the method of the present invention provided oxy-diphthalic anhydrides of the product with the higher yield and the simpler reaction.

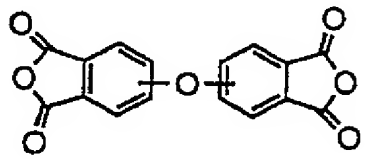
CLAIMS

1. A method for preparing oxy-diphthalic anhydrides, which comprises reacting a halo-phthalic anhydride represented by the formula (1):



(1)

where Hal represents F, Cl, Br or I,
with a carbonate salt selected from the group consisting of lithium carbonate, sodium carbonate, magnesium carbonate and calcium carbonate in a solvent to prepare oxy-diphthalic anhydrides represented by the formula (2):



(2)

2. The method according to Claim 1, wherein said carbonate salt is a granular sodium carbonate or lithium carbonate having the diameter of 50-750 μm.

3. The method according to Claim 1 or 2, wherein said reaction is carried out in the presence of a phosphonium or sulfonium salt which acts as a phase transfer catalyst.

4. The method according to Claim 3, wherein said reaction is carried out in the presence of an alkali-metal iodide or fluoride which acts as a co-catalyst.

5. The method according to Claim 4, wherein said alkali-metal iodide is selected from the group consisting of lithium iodide, sodium iodide and potassium iodide.

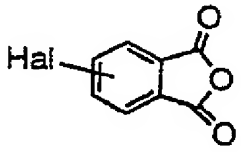
6. The method according to Claim 4, wherein said alkali-metal fluoride is selected from the group consisting of lithium fluoride, sodium fluoride and potassium fluoride.

7. The method according to any one of Claims 1-6, wherein said reaction is carried out at the temperature of 170-260°C.

AMENDED CLAIMS

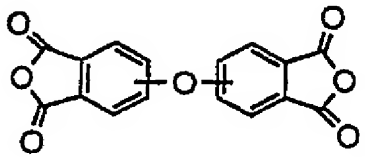
[received by the International Bureau on 25 March 1999 (25.03.99);
original claims 1-7 replaced by amended claims 1-6 (2 pages)]

1. A method for preparing oxy-diphthalic anhydrides, which comprises reacting a halo-phthalic anhydride represented by the formula (1):



(1)

where Hal represents F, Cl, Br or I,
with a carbonate salt selected from the group consisting of lithium carbonate, sodium carbonate, magnesium carbonate and calcium carbonate in a solvent, in the presence of a phosphonium or sulfonium salt which acts as a phase transfer catalyst, to prepare oxy-diphthalic anhydrides represented by the formula (2):



(2)

2. The method according to Claim 1, wherein said carbonate salt is a granular sodium carbonate or lithium carbonate having the diameter of 50-750 μm.

3. The method according to Claim 1 or 2, wherein said reaction is carried out in the presence of an alkali-metal iodide or fluoride which acts as a co-catalyst.

4. The method according to Claim 3, wherein said alkali-

metal iodide is selected from the group consisting of lithium iodide, sodium iodide and potassium iodide.

5. The method according to Claim 3, wherein said alkali-metal fluoride is selected from the group consisting of lithium fluoride, sodium fluoride and potassium fluoride.

6. The method according to any one of Claims 1-5, wherein said reaction is carried out at the temperature of 170-260°C.

STATEMENT UNDER ARTICLE 19

The method as claimed in amended Claim 1 of the present application includes the use of a phosphonium or sulfonium salt which acts as a phase transfer catalyst and does not include the use of a nitrite salt. On the other hand, the method as disclosed in JP 55 127343 A (MITSUI TOATSU CHEMICALS INC.) cited as category X includes the use of a nitrite salt and does not include the use of a phosphonium or sulfonium salt. Thus, a reaction system of the method as amended Claim 1 of the present application is essentially distinct from that of JP 55 127343 A.

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/JP 98/05390

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C51/567

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 8046 Derwent Publications Ltd., London, GB; AN 80-81647C XP002091411 & JP 55 127343 A (MITSUI TOATSU CHEMICALS INC.), 2 October 1980 see abstract	1
A	US 5 021 168 A (MOLINARO ET. AL.) 4 June 1991 see claims; examples	1-7
A	US 5 153 335 A (STULTS) 6 October 1992 see column 2, line 39 - column 5, line 15; claims	1-7

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 January 1999	10/02/1999

Name and mailing address of the ISA	Authorized officer
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Int ional Application No
PCT/JP 98/05390

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 264 624 A (OCCIDENTAL CHEMICAL CORPORATION) 27 April 1988 see claims; examples	1-7

2

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte onal Application No
PCT/JP 98/05390

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP 63096183 A	27-04-1988

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Ｂ０１Ｊ 31/30		Ｂ０１Ｊ 31/30	Ｚ
// Ｃ０７Ｂ 61/00	３００	Ｃ０７Ｂ 61/00	３００

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(33)優先権主張国　日本（ＪＰ）
早期審査対象出願
前置審査

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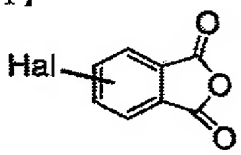
最終頁に続く

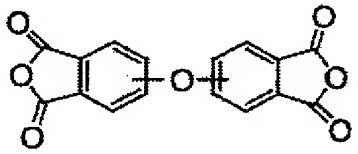
(54)【発明の名称】　オキシジフタル酸無水物の製造方法

(57)【特許請求の範囲】
【請求項１】　式１
【化１】



(1)

（式中、Ｈａｌは Ｆ、Ｃｌ、Ｂｒ又はＩを表す）のハロ無水フタル酸と、炭酸リチウム、炭酸ナトリウム、炭酸マグネシウム及び炭酸カルシウムから選ばれる粒状炭酸塩とを、溶媒中で反応させ（ここで、該溶媒は、ハロ無水フタル酸に対して５０～２００重量%である）、
式２
【化２】



(2)

で示されるオキシジフタル酸無水物を製造する方法。
【請求項２】　炭酸塩が、粒径５０～７５０μｍの粒状炭酸ナトリウム又は粒状炭酸リチウムである、請求項１記載の方法。
【請求項３】　相間触媒であるホスホニウム塩又はスルホニウム塩の存在下で反応させる、請求項１又は２記載の方法。
【請求項４】　さらにアルカリ金属ヨウ化物又はアルカリ金属フッ化物の助触媒の存在下で反応させる、請求項３記載の方法。

【請求項５】　アルカリ金属ヨウ化物が、ＬｉＩ、ＮａＩ及びＫＩから選ばれる請求項４記載の方法。

【請求項６】　アルカリ金属フッ化物が、ＬｉＦ、ＮａＦ及びＫＦから選ばれる請求項４記載の方法。

【請求項７】　１７０～２６０℃の反応温度で反応させる、請求項１～６のいずれか１項記載の方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、オキシジフタル酸無水物の製造方法に関する。オキシジフタル酸無水物は、各種ジアミンと反応させてポリイミドを製造する原料として重要である。

【０００２】

【従来の技術及び発明が解決しようとする課題】オキシジフタル酸無水物の種々の製造方法が文献に記載されている。古くは、Marvelらによるテトラメチルフェニルエーテルの酸化反応による製法がある（J. Am. Cherm. Soc. 80, 1197-(1955)）。この酸化反応は、酸化剤として毒性の強い過マンガン酸カリウムを使用するため、工業的な製法には不適である。また、特開昭５３－１２２７３８号公報には、ハロ無水フタル酸とカセイソーダを極性溶媒中で反応させて、オキシジフタル酸無水物を得る方法が記載されているが、この反応での目的物の収率は極めて低い。特開昭５５－１３６２４６号及び特開昭５５－１２７３４３号公報には、ニトロ無水フタル酸と亜硝酸ソーダ並びに炭酸塩を極性溶媒中で反応させてオキシジフタル酸無水物を製造する方法が記載されている。これらの製法では、反応中に有害な酸化窒素が副生するため、工業的には利用しにくい。

【０００３】特開昭６３－９６１８３号公報には、極性溶媒中でハロ無水フタル酸と炭酸カリウム及びフッ化カリウム又はフッ化セシウムとを反応させるオキシジフタル酸無水物の製造方法が開示されているが、この方法は水が介在する反応であり、水が存在すると反応率が低下して十分な収率が得られない。

【０００４】特公平３－５００７１号公報には、ヒドロキシ無水フタル酸とハロ無水フタル酸とを、炭酸カリウムの存在下に脱ハロゲン化水素反応させてオキシジフタル酸無水物を得る方法が開示されている。この方法はヒドロキシ無水フタル酸をハロ無水フタル酸の加水分解により製造しなければならず、工業的に有利な製法とは言えない。

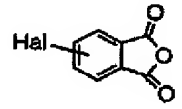
【０００５】特開平１－２５４６７３号公報には、ハロ無水フタル酸と炭酸カリウムを、フッ化カリウム触媒の存在下に反応させて、直接オキシジフタル酸無水物を製造する方法が開示されている。この方法はニート反応あるいはニートに近い反応であるため、撹拌方法に工夫が必要であり、安定した反応性を得ることが難しい。しかもこの方法は炭酸カリウムの使用に限定され、他の炭酸塩類、例えば炭酸ナトリウムでこの方法をトレースすると、反応物の粘度が高くなり、十分な流動性が得られずに反応が途中で停止してしまう。

【０００６】

【課題を解決するための手段】本発明の方法は、式１

【０００７】

【化３】

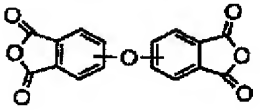


（１）

【０００８】（式中、ＨａｌはＦ、Ｃｌ、Ｂｒ又はＩを表す）のハロ無水フタル酸と、炭酸リチウム、炭酸ナトリウム、炭酸マグネシウム及び炭酸カルシウムから選ばれる炭酸塩とを、溶媒中で反応させ、式２

【０００９】

【化４】



（２）

【００１０】で示されるオキシジフタル酸無水物を製造する方法である。

【００１１】

【発明の実施の形態】本発明では、炭酸カリウム以外の炭酸塩及び溶媒を利用して反応させてオキシジフタル酸無水物を製造することができる。炭酸塩の形状は粉末でも粒状でもよいが、好ましくは粒状の炭酸塩を使用すると効率よく反応させることができる。例えば、通常ソーダ灰と称される粒状炭酸ナトリウムを使用した場合、反応率９０％で目的物が得られることがわかった。

【００１２】使用されうる炭酸塩としては、炭酸リチウム、炭酸ナトリウム、炭酸マグネシウム及び炭酸カルシウムより選ばれるが、好ましくは炭酸ナトリウムである。炭酸カリウムを使用して溶媒中で反応させると、反応が途中で停止し、所定の反応率を得ることができない。本発明の方法で用いる炭酸塩の形態は粉末、粒状どちらでもかまわないが、好ましくは粒径が５０～７５０μｍ、さらに好ましくは１５０～７５０μｍの粒状炭酸塩である。該炭酸塩とハロ無水フタル酸のモル比は、約０．５近傍が収率の点から有利であるが、好ましいモル比は０．５～０．４である。

【００１３】本発明の方法が実施される反応温度は、一般に１７０～２６０℃の範囲で行われる。使用する触媒は、反応温度に耐えうる相関触媒である、ホスホニウム塩、スルホニウム塩が利用できる。例えばトリフェニルホスフィン、臭化テトラフェニルホスホニウム、塩化テトラブチルホスホニウム、ヨウ化トリエチルスルホニウム、臭化トリフェニルスルホニウムなどである。触媒量は、ハロ無水フタル酸に対し０．１～１０重量％、好ましくは０．３～５重量％である。また、アルカリ金属ヨ

ウ化物又はアルカリ金属フッ化物を助触媒として使用することにより反応性を高めることができ、しかも製品の着色が少ない利点もある。使用されるアルカリ金属ヨウ化物としては、ＬｉＩ、ＮａＩ、ＫＩ、アルカリ金属フッ化物としては、ＬｉＦ、ＮａＦ、ＫＦなどが挙げられる。使用量はハロ無水フタル酸に対して０．０５～５重量%、好ましくは０．１～２重量%である。

【００１４】反応には、溶媒を用いる。使用する溶媒は、反応温度（１７０～２６０℃）付近に沸点を持ち、反応に関与しないものでなければならない。例えば、１，２－ジクロロベンゼン、１，２，４－トリクロロベンゼンのようなポリ塩化ベンゼン、１，２－ジクロロトルエンのようなポリ塩化トルエンが使用可能である。脱水された非プロトン性の極性溶媒、例えばスルホランも使用可能である。使用量はハロ無水フタル酸に対して５０～６００重量%、好ましくは１００～２００重量%である。

【００１５】オキシジフタル酸無水物を単離するには、反応生成物を熱時濾過し得られる濾液を冷却し、オキシジフタル酸無水物を得る。必要に応じて濾液を濃縮し、収量アップをはかる。またスルホランの場合、濾液を水に分散させ、析出するオキシジフタル酸を固液分離する。得られたオキシジフタル酸を加熱又は無水酢酸を使用して閉環し、オキシジフタル酸無水物を得る。

【００１６】本発明の方法では、溶媒存在下にて反応させるため、ニート反応に比べて樹脂成分が生成しにくく、着色しにくいため、脱色精製の負担を軽減できる。したがって、高純度が要求される電子材料用途にも好適なオキシフタル酸無水物を得ることができる。

【００１７】

【実施例】実施例１

４－ブロモ無水フタル酸９０．８ｇ（０．４mol)及び１，２－ジクロロトルエン１５０ｇを反応器に入れ、２１０℃に加熱した。次に粒径２００～５００μmの粒状炭酸ナトリウム２１．２ｇ（０．２０mol)、臭化テトラフェニルホスホニウム４．５ｇ（０．０１１mol)、及びヨウ化カリウム２．１ｇ（０．０１３mol)を９０分間にわたって分割投入した。投入後３時間熟成させた。生成物を高速液体クロマトグラフでチェックすると、反応率９０%であった。反応物を冷して１５０℃に下げ、熱時濾過した。濾液を冷却後、４－オキシジフタル酸無水物を単離した。収量５０．９ｇ（収率８２．０%）。さら＊

＊に精製を必要とするときは酢酸洗浄する。

【００１８】実施例２

３－クロロ無水フタル酸７３．０ｇ（０．４０mol)及び１，２，４－トリクロロベンゼン２００ｇを反応器に入れ、２２０℃に加熱した。次に粒径２００～５００μmの粒状炭酸リチウム１４．８ｇ（０．２０mol)、ヨウ化トリエチルスルホニウム３．５ｇ（０．０１５mol)、及びフッ化カリウム１．８ｇ（０．０３１mol)を９０分間にわったって分割投入した。投入後４時間熟成させた。生成物を高速クロマトグラフでチェックすると、反応率８８%であった。反応物を冷して１５０℃に下げ、熱時濾過した。濾液を冷却後、３－オキシジフタル酸無水物を単離した。収量４９．６ｇ（収率７９．９%）。さらに精製を必要とするときは酢酸洗浄する。

【００１９】実施例３

４－ブロモ無水フタル酸９０．８ｇ（０．４０mol)及び脱水スルホラン１５０ｇを反応器に入れ、２００℃に加熱した。次に粒径２００～５００μm の粒状炭酸ナトリウム２１．２ｇ（０．２０mol)、トリフェニルホスフィン４．５ｇ（０．０１７mol)、及びヨウ化カリウム２．１ｇ（０．０１３mol)を９０分間にわたって分割投入した。投入後４時間熟成させた。生成物を高速液体クロマトグラフでチェックすると、反応率８５%であった。反応物を冷して１５０℃に下げ、熱時濾過した。濾液を冷却後、５%酢酸水溶液５００ml中へ入れ、９０℃で２時間加熱撹拌し、オキシジフタル酸無水物を開環させ、テトラカルボン酸とした。冷却後、固液分離し、得られたオキシジフタル酸を１，２－ジクロロベンゼン２００ｇ中で、２２０℃で３時間加熱閉環させた。オキシジフタル酸の閉環が終了すると系内は白濁から透明～少し濁った状態に変わる。これを熱時濾過し、濾液を冷却後、４－オキシジフタル酸無水物を単離した。収量４９．０ｇ（収率７９．０%）。さらに精製を必要とするときは酢酸洗浄する。

【００２０】比較例１

実施例１における粒状炭酸ナトリウムの代りに、粒径２００～５００μm の粒状炭酸カリウムを用いた以外は、同様の条件で反応させた。４－オキシジフタル酸無水物の収率は３７．１%であり、溶媒中の炭酸カリウムとの反応に比べて、本発明の方法では高収率かつ容易な反応で目的物のオキシジフタル酸無水物が得られた。

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